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A Study of the Structure of Grain Boundaries in Polycrystalline Magnesium Oxide

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Abstract

The structure of the grain boundary in a typical polycrystalline ceramic (MgO) is described in terms of a random network. The development is based on the existence of variable coordination of both species in the structure to permit a stable random network. The theory first develops the energy relationship and coordination distribution in such a network in a stress-free homogeneous environment and then considers the distribution that might exist in a gradient occurring at a discontinuity (grain boundary or free surface).

The results suggest that such an approach is capable of describing the conditions at disordered regions in an ordered structure. It appears that the method could be more rigorously developed if needed and, in that case, could be applied to more complex ceramics and used to describe temperature–viscosity relationships in such networks. Finally, the theory indicates that in a theoretically pure MgO, the thickness of the random network at a free surface would be of the order of 2–3 atomic distances, and the total thickness of a grain boundary, of the same order of magnitude.

A Study of the Structure of Grain Boundaries in Polycrystalline Magnesium Oxide

I. Introduction

No completely satisfactory description exists for grain boundaries in ionic materials, either in terms of a random misfit of two grains or in terms of specific dislocation patterns. Analysis of the problem suggested that some of the random network ideas useful in describing silicate networks might have application here in describing specifically the structure of the grain boundaries. Although such a network, in the absence of any glass-forming oxides, would normally be considered a model for a low-viscosity liquid with very little stability below the melting point (or liquidus in the case of mixed oxides) it will be shown that such a liquid, in very thin layers between two crystalline grains, can have stability at temperatures below the melting point. Magnesium oxide has been selected because of the interest at the Jet Propulsion Laboratory in the forming and hot-pressing of this material and also because the simple RO-type formula simplifies analysis. However, the methods developed will be perfectly applicable to more complicated formulas or to mixed oxides.

In these studies, an effort is made to express the ideas in quantitative form and to attempt to make deductions on orders of magnitude of such quantities as surface tension and grain boundary thickness. Since this is a preliminary study, no effort is made to treat the forces between ions as rigorously as is frequently done in calculating properties of ionic materials.

II. Description of the Model

A. The Meaning of "Random Network"

Some single oxides, when melted and cooled, readily form glasses. In general, in the crystalline form of such oxides, each cation is surrounded by a small number of oxygens and each oxygen is attached to (or bridges between) two and only two cations. Silica, for instance, in the high-temperature form (cristobalite), has each silicon surrounded by four oxygens and each oxygen bridging between two silicons. The silicons and the oxygens form six-member rings in which six silicons and six oxygens alternate. It is possible to rearrange this type of crystal structure into a random structure where each cation still has the same number of oxygens and each oxygen still bridges between two cations. One way of describing the randomness of such a structure would be to say that instead of all the rings in the structure having six silicons and six oxygens, some may have four, five, seven, or some other number arranged in a random manner.

The presence of such a glass-forming oxide (even in amounts of less than 50% in some cases) in melts containing several oxides can still promote easy glass formation. One plausible way of describing the structure of such glasses is to assume that the cation of the glass-forming oxide always enters the structure with the same coordination number, while other cations may fit into the structure with a somewhat variable coordination number. Unpublished studies by one of the authors (HTS) of the densities of simple silicate glasses indicate that this leads to results consistent with measured densities of a large number of glasses. The larger the cation and the smaller its charge, the greater will be the variability of its coordination.

It seems a logical step to postulate that when no glass-forming oxide is present, it is still possible to have a random network by allowing each cation and each anion to enter into the structure with a varying coordination number. Figure 1 illustrates this concept in a two-dimensional drawing, which could very well describe the structure of molten magnesium oxide. The ease with which an ion could change its surroundings would be associated with the rather high fluidity characteristic of melts containing litle or no silica or other glass-former. The methods developed below could, incidentally, easily be extended to allow calculation of viscosities and their temperature dependence. This calculation is not attempted here.

This random structure might also be used to describe the structure of grain boundaries in the thin layer between two crystal grains of different orientation. One of the main purposes of this study is to investigate how such a "liquid" structure could be in equilibrium with two crystals at a temperature below the melting point of the crystals. It is first necessary to develop the network model under the influence of hydrostatic conditions

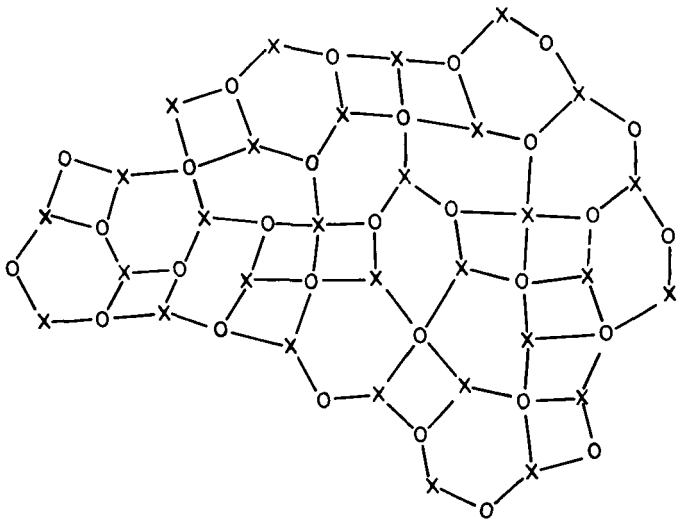

Fig. 1. Two-dimensional representation of a random network

and then to consider the influence of a gradient as it might exist at a discontinuity. The network development is contained in the rest of Section II, while the influence of the discontinuity is considered in Section III.

In order to begin to make some predictions about the equilibrium behavior of such a liquid, it is necessary to be able to calculate, for any postulated distribution of coordination numbers, the energy, entropy, and volume of one mole or any other specified quantity. In all the calculations, the thermal energy and entropy arising from lattice or network vibrations are completely neglected. The temperatures are very high and most of the Einstein functions entering into thermal capacity calculations are very close to unity. The differences between vibrational energies of two different structures (even crystal and liquid) would be small compared with differences in structural energies.

B. Entropy of a Random Network

The network will consist of an assembly of cations and anions that may have coordinations of 2 to 12. This range will be considerably reduced when numerical calculations are attempted. Let there be, in one mole of MgO,

n_2 moles of cations in 2-fold coordinates

n_3 moles of cations in 3-fold coordinates

.
.
.

n_{12} moles of cations in 12-fold coordinates

and

q_2 moles of anions in 2-fold coordinates

q_3 moles of anions in 3-fold coordinates

$\vdots$

q_{12} moles of anions in 12-fold coordinates

where

$$\sum_i n_i = 1 \text{ and } \sum_i q_i = 1$$

Then, if N is Avogadro's number, it is assumed that the entropy S of one mole of MgO can be written

$$S = k \ln \left(\frac{N!}{n_2 N! \, n_3 N! \cdots n_{12} N!} \, \frac{N!}{q_2 N! \, q_3 N! \cdots q_{12} N!} \right)$$

which, through the use of Stirling's approximation, can be written

$$\begin{aligned} S = k(&N \ln N - n_2 N \ln n_2 N - n_3 N \ln n_3 N - \cdots - n_{12} N \ln n_{12} N \\ &+ N \ln N - q_2 N \ln q_2 N - q_3 N \ln q_3 N - \cdots - q_{12} N \ln q_{12} N) \end{aligned}$$

or

$$S = R(-n_2 \ln n_2 - n_3 \ln n_3 - \cdots - n_{12} \ln n_{12} - q_2 \ln q_2 - q_3 \ln q_3 - \cdots - q_{12} \ln q_{12})$$

where k is Boltzmann's constant and R is the gas constant. The units will be calories per mole per degree C if R is expressed in these units.

C. Energy of a Random Network

In an ionic structure, a large part of the structural energy is the Coulomb energy, which can be written in the form

$$\frac{1}{2} \sum_i \phi_i e_i$$

where e_i is the charge in ion i and ϕ_i is the potential at the site of ion i arising from all of its neighbors. This quantity is always negative, since the potential at each ion site always comes out opposite in sign to the charge in the ion occupying the site. The energy so described represents the amount by which the Coulomb energy of the structure is less than the energy of the ions all infinitely separated from each other.

Calculation of the value of ϕ at each ion site is, for a crystal, an important and somewhat difficult step in the usual calculation of the Madelung constant of the crystal. For crystals of the RO type, the numerical value of the Madelung constant (expressed in terms of closest cation–anion separation) is the same number as ϕ expressed as a multiple of e^2/r, where e is the charge on either ion and r is the cation–anion separation. The assumption is then made that the average value of ϕ at the site of an ion in a random network can be read from a curve of Madelung constants for known crystal structures. In order to get a more complete curve, a Madelung constant was calculated as 1.387 for a single chain of alternating positive and negative charges (coordination 2), as 1.000 for an assembly of isolated diatomic molecules (coordination 1), and as 0.000 for a well dispersed gas of separate ions (coordination zero). The values used in drawing the curve are shown in Table 1 and are plotted in Fig. 2.

Table 1. Values of Madelung constant for RO-type structures with different coordination numbers

Coordination number	Model	Madelung constant
0	Ionic gas	0.000
1	Diatomic molecules	1.000
2	Linear chain	1.387
4	ZnS	1.640
6	NaCl	1.748
8	CsCl	1.763

That this is a valid method for calculating energies of a network is illustrated in Appendix A by calculating from these values the Madelung constant for completely different crystal structures, such as fluorite, rutile, and corundum.

The effect of the randomness on such a calculation is discussed in Appendix B.

It is not possible to discuss the "correct" coordination number for a cation without also introducing the high-order repulsion terms that also enter, since they largely control the number of anions surrounding a cation. If an exponent of 7 is used in the denominator of the repulsion term, then the energy per mole of each kind of ion can be calculated, and the results, for MgO, are as shown in Table 2 (counting only 6-fold, 5-fold, 4-fold, 3-fold, and 2-fold ions). These energies have been arbitrarily adjusted to make the 6-fold ions have zero energy.

Table 2. Energy of ions in MgO as a function of coordination number

Type of ion	Energy per mole, kcal
6-fold	0.00
5-fold	−0.95
4-fold	1.74
3-fold	9.17
2-fold	22.99

The numbers in Table 2 are for the energy of magnesium ions. In the numerical calculations to follow, it was assumed that these numbers could also be applied to the oxygen ions. This is obviously incorrect, since there is no difficulty in putting even more than six magnesium ions around an oxygen ion. In a more rigorous treatment, the oxygens would be treated separately. The assumption was made merely to simplify the calculations and does not represent an inherent limitation on the treatment. This will be made clearer in the treatment of the free energy of the network.

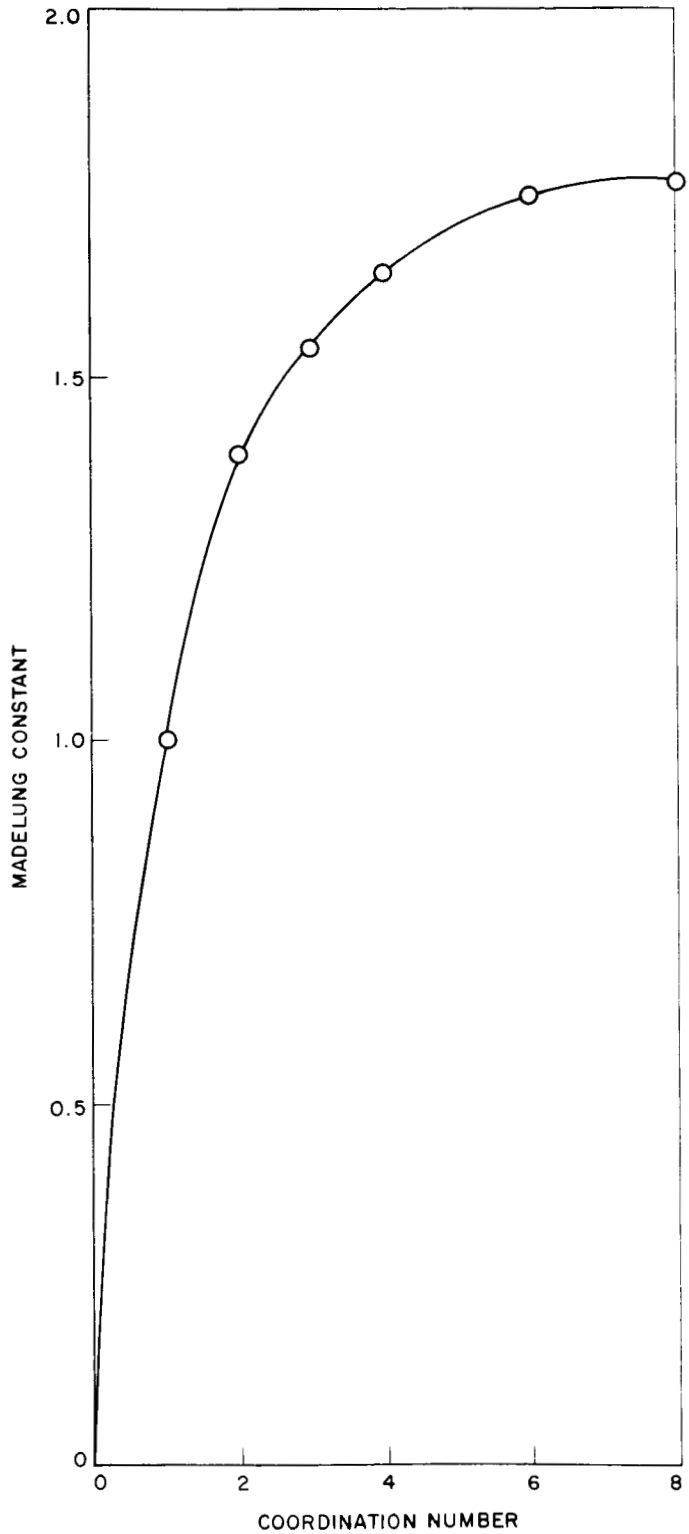

Fig. 2. Madelung constant of RO-type crystal as a function of coordination number

D. Volume of a Random Network

A method of arriving at a value for the volume of a random network may be borrowed from work being done in silicate networks. Each ion of one kind is surrounded by a certain number of ions of the opposite kind. If planes are constructed that perpendicularly bisect each of the straight lines from this central ion to each of its neighbors, the ion will be enclosed in a polyhedron of as many faces as the ion has neighbors. Every ion in the structure may be surrounded by such polyhedra, and they should account for all the space occupied by the structure. This holds except for ions surrounded by only two or three ions of the opposite kind, since the polyhedra in these cases are not closed. They can, however, be treated separately, as will be shown.

Each polyhedron consists of a number of pyramids, with all their points coming together at the enclosed ion. In calculating the volume, these pyramids are replaced by right circular cones whose height from base to apex is one-half the bond length and whose total solid angles add up to 4π. If the number of such cones around an ion is n, then it can be shown that the total volume occupied by the n cones is

$$\frac{4\pi r^3}{3}\frac{n(n-1)}{(n-2)^2}$$

where r is one-half the bond length. As n increases, the polyhedron approaches a sphere in shape and the volume approaches $(4\pi r^3)/3$.

A difficulty arises in the case of ions with only two or three neighbors, since the polyhedron in either of these cases is not a closed figure. The value for a 2-fold ion was taken by considering vitreous silica, whose molar volume is 27.26 cm^3. The volume of the silicons, in 4-fold coordinates, can be computed, and the difference, which actually accounts for most of the volume, is assigned to the 2-coordinated oxygens. A smooth curve joining this value to the other allows an interpolation giving the value for ions in 3-fold coordinates. The number plotted in this case is the factor used to multiply the cube of one-half the bond length to get the volume in cm^3 per mole.

The one-half bond length r itself varies with coordination number. If, again, an exponent of 7 is assumed in the denominator of the repulsive term, then it is a reasonable assumption that r varies as the one-sixth power of the coordination number. If a value of 2.1 Å is taken for a coordination number of 6, then the volumes for the different kinds of ions can be calculated as shown in Table 3. Again, in the interest of simplification, the calculations are assumed to apply also to the oxygen ions. It would probably be more correct to divide the MgO bond always at a fixed distance from the oxygen and vary the rest of the bond length according to the coordinates of the magnesium. However, for initial simplicity, the simple procedure described above was used.

Table 3. Volume of ions in MgO as a function of coordination number

Coordination number	Volume of ion, cm^3 per mole
2	16.796
3	11.907
4	8.200
5	6.458
6	5.614

E. Free Energy of a Random Network

In order to understand the equilibrium behavior of such a body, either in the absence of stress or in the presence of such stress as necessarily enters at a density discontinuity, it is necessary to set up a free energy function $G = E + PV - TS$ and minimize it by properly choosing the independently adjustable parameters. This free energy function will be kept as general as possible until the actual numerical calculations are attempted. Both the magnesium and oxygen ions will have coordination numbers from 2 to 12. The energies of the magnesium ions will be denoted $\alpha_2, \alpha_3, \alpha_4, \cdots \alpha_{12}$, and the energies of the oxygens, $\alpha'_2, \alpha'_3, \alpha'_4, \cdots \alpha'_{12}$; the subscript denotes the coordination number of the ion. The volumes of the magnesium ions will be $v_2, v_3, v_4 \cdots v_{12}$, and of the oxygens, $v'_2, v'_3, v'_4, \cdots v'_{12}$. The values for α will be in calories per mole and those for v, in cm^3 per mole.

If pressure is measured in dynes per cm^2, then the PV term in the free energy will be of the form

$$\frac{P}{W}\left(\sum_i n_i v_i + \sum_i q_i v'_i\right)$$

where W is the mechanical equivalent of heat in ergs per calorie. All energy units are then in calories per mole.

The free energy function G can then be written

$$G = \sum_i n_i\alpha_i + \sum_i q_i\alpha'_i + \frac{P}{W}\left(\sum n_i v_i + \sum q_i v'_i\right) + RT\left(\sum n_i \ln n_i + \sum q_i \ln q_i\right)$$

Not all the n and q terms are independent. They satisfy the three relations

$$\sum_i n_i = 1$$

$$\sum_i q_i = 1$$

$$\sum_i i n_i = \sum_i i q_i$$

The third relation simply states that the number of bonds going out from the magnesiums is equal to the number of bonds going to the oxygens. Three of the n and q terms, then, are not independent of the others. If these are taken as n_2, n_3, and q_2, then the three relations above can be solved for n_2, n_3, and q_2 as follows:

$$q_2 = 1 - q_3 - q_4 - \cdots - q_{12}$$

$$n_2 = 1 - q_3 - 2q_4 - \cdots - 10q_{12} + n_4 + 2n_5 + \cdots + 9n_{12}$$

$$n_3 = q_3 + 2q_4 + \cdots + 10q_{12} - 2n_4 - 3n_5 - \cdots - 10n_{12}$$

The free energy function G may be minimized by expressing the relations that the partial derivatives of G with respect to each of the n terms from n_4 to n_{12} and each of the q terms from q_3 to q_{12} is zero. The derivatives with respect to n take the form

$$\frac{\partial G}{\partial n_4} = \alpha_2 - 2\alpha_3 + \alpha_4 + \frac{P}{W}(v_2 - 2v_3 + v_4) + RT(\ln n_2 - 2\ln n_3 + \ln n_4) = 0$$

$$\frac{\partial G}{\partial n_5} = 2\alpha_2 - 3\alpha_3 + \alpha_5 + \frac{P}{W}(2v_2 - 3v_3 + v_5) + RT(2\ln n_2 - 3\ln n_3 + \ln n_5) = 0$$

$$\vdots$$

$$\frac{\partial G}{\partial n_{12}} = 9\alpha_2 - 10\alpha_3 + \alpha_{12} + \frac{P}{W}(9v_2 - 10v_3 + v_{12}) + RT(9\ln n_2 - 10\ln n_3 + \ln n_{12}) = 0$$

The first of these equations can be rewritten as follows:

$$\alpha_4 - \alpha_3 + \frac{P}{W}(v_4 - v_3) + RT(\ln n_4 - \ln n_3) = \alpha_3 - \alpha_2 + \frac{P}{W}(v_3 - v_2) + RT(\ln n_3 - \ln n_2)$$

Subtracting the first from the second yields

$$\alpha_5 - \alpha_4 + \frac{P}{W}(v_5 - v_4) + RT(\ln n_5 - n_4) = \alpha_3 - \alpha_2 + \frac{P}{W}(v_3 - v_2) + RT(\ln n_3 - \ln n_2)$$

and by subtracting them in pairs, one obtains the whole series of similar equations ending with

$$\alpha_{12} - \alpha_{11} + \frac{P}{W}(v_{12} - v_{11}) + RT(\ln n_{12} - \ln n_{11}) = \alpha_2 - \alpha_2 + \frac{P}{W}(v_3 - v_2) + RT(\ln n_3 - \ln n_2)$$

It is convenient to set

$$A = \alpha_3 - \alpha_2 + \frac{P}{W}(v_3 - v_2) + RT(\ln n_3 - \ln n_2)$$

where A is as yet undetermined.

While it is difficult to describe the exact physical meaning of this constant A, it is a measure of the difference in behavior of the cations on the one hand and the anions on the other. If they behave in exactly the same manner, A is zero. In any case, as will be evident later, with the assumptions that have been made, A can be uniquely determined in each case. The equations above can then be put in the form shown below:

$$\frac{n_2}{n_3} = \exp\left[-\frac{\alpha_2 - \alpha_3}{RT} - \frac{P(v_2 - v_3)}{WRT}\right]\exp(-A/RT)$$

$$\frac{n_3}{n_4} = \exp\left[-\frac{\alpha_3 - \alpha_4}{RT} - \frac{P(v_3 - v_4)}{WRT}\right]\exp(-A/RT)$$

$$\vdots$$

$$\frac{n_{11}}{n_{12}} = \exp\left[-\frac{\alpha_{11} - \alpha_{12}}{RT} - \frac{P(v_{11} - v_{12})}{WRT}\right]\exp(-A/RT)$$

If A were known, these equations, along with the relation $\Sigma n_i = 1$, would uniquely determine the n terms.

The partial derivatives of G with respect to q can be expressed as follows:

$$\frac{\partial G}{\partial q_3} = -\alpha_2 + \alpha_3 - \alpha_2' + \alpha_3' + \frac{P}{W}(-v_2 + v_3 - v_2' + v_3') + RT(-\ln n_2 + \ln n_3 - \ln q_2 + \ln q_3) = 0$$

$$\frac{\partial G}{\partial q_4} = -2\alpha_2 + 2\alpha_3 - \alpha_2' + \alpha_4' + \frac{P}{W}(-2v_2 + 2v_3 - v_2' + v_4') + RT(-2\ln n_2 + 2\ln n_3 - \ln q_2 + \ln q_4) = 0$$

$$\vdots$$

$$\frac{\partial G}{\partial q_{12}} = -10\alpha_2 + 10\alpha_3 - \alpha_2' + \alpha_{12}' + \frac{P}{W}(-10v_2 + 10v_3 - v_2' + v_{12}') + RT(-10\ln n_2 + 10\ln n_3 - \ln q_2 + \ln q_{12}) = 0$$

If, as before,

$$\alpha_3 - \alpha_2 + \frac{P}{W}(v_3 - v_2) + RT(\ln n_3 - \ln n_2) = A$$

then the relations above can be expressed in the following form:

$$\frac{q_2}{q_3} = \exp\left[-\frac{\alpha_2' - \alpha_3'}{RT} - \frac{P(v_2' - v_3')}{WRT}\right]\exp(A/RT)$$

$$\frac{q_3}{q_4} = \exp\left[-\frac{\alpha_3' - \alpha_4'}{RT} - \frac{P(v_3' - v_4')}{WRT}\right]\exp(A/RT)$$

$$\vdots$$

$$\frac{q_{11}}{q_{12}} = \exp\left[-\frac{\alpha_{11}' - \alpha_{12}'}{RT} - \frac{P(v_{11}' - v_{12}')}{WRT}\right]\exp(A/RT)$$

F. Coordination Population of a Random Network

The relations that have been developed can be used to determine uniquely the n and q terms. Any arbitrary value is assigned to A, which is as yet unknown, and the ratios of the q's to each other and of the n's to each other are calculated. The q and the n terms are then adjusted so that

$$\sum_i n_i = 1$$

$$\sum_i q_i = 1$$

If the correct value of A has been chosen, then, in addition,

$$\sum i n_i = \sum i q_i$$

If this is not satisfied, then other values of A are tried until it is. In this way, one can calculate the distribution of n and q terms for a stress-free state or any state of hydrostatic pressure (or tension). The calculations emphasize an important difference between such a liquid and a crystal. The crystal can change its volume only by changes in the interionic distances. The liquid can change its volume by structural changes to higher or lower average coordination numbers, which, in general, means that the compressibility of the liquid will be enormously greater.

In order to get some preliminary feeling for orders of magnitude, completely symmetrical behavior of the magnesiums and the oxygens was assumed. This implies that $\alpha_2 = \alpha'_2$, $\alpha_3 = \alpha'_3$, $\alpha_4 = \alpha'_4$, and so on, and also that $v_2 = v'_2$, $v_3 = v'_3$, $v_4 = v'_4$, and so on. The equations are perfectly capable of handling any much more general (and more plausible) case, but as a first attempt this oversimplification was made. It means that the A in the relations determining the n and q terms is zero. The previous values for α (Table 2) and v (Table 3) were used.

In the calculations in the next section, it is necessary to know the n values (in moles per unit volume) for a wide range of tensions and pressures in order to discuss conditions close to a discontinuity (free surface or liquid–crystal interface). In this case, the ratios

$$\frac{n_2}{n_3}, \frac{n_3}{n_4}, \frac{n_4}{n_5}, \frac{n_5}{n_6}$$

are calculated as described above, and then the absolute values are adjusted so that

$$2(n_2v_2 + n_3v_3 + n_4v_4 + n_5v_5 + n_6v_6) = 1$$

The factor of 2 enters because the n terms now describe not only the state of the magnesiums but also that of the

Table 4. Ionic populations in MgO for different pressures

Pressure, bars	Amount, moles/cm³, for indicated ion type and direction of pressure									
	Tension					Compression				
	n_6	n_5	n_4	n_3	n_2	n_6	n_5	n_4	n_3	n_2
0	.02535	.03425	.01460	.00138	.00002	.02535	.03425	.01460	.00138	.00002
10	.02414	.03369	.01533	.00175	.00002	.02650	.03469	.01384	.00113	.00002
20	.02300	.03315	.01612	.00201	.00004	.02764	.03504	.01309	.00094	.00001
30	.02181	.03245	.01686	.00243	.00005	.02876	.03532	.01234	.00076	.00001
40	.02060	.03165	.01757	.00291	.00007	.02988	.03554	.01163	.00062	.00000
50	.01938	.03074	.01823	.00348	.00011	.03098	.03568	.01093	.00051	.00000
60	.01814	.02971	.01883	.00414	.00016	.03207	.03576	.01025	.00042	.00000
70	.01690	.02858	.01934	.00490	.00022	.03314	.03579	.00961	.00034	.00000
80	.01564	.02732	.01976	.00575	.00032	.03420	.03577	.00899	.00028	.00000
90	.01438	.02594	.02004	.00671	.00045	.03525	.03571	.00840	.00023	.00000
100	.01313	.02444	.02017	.00778	.00062	.03628	.03560	.00783	.00018	.00000
110	.01188	.02283	.02013	.00894	.00086	.03731	.03546	.00730	.00015	.00000
120	.01063	.02109	.01987	.01016	.00118	.03831	.03527	.00680	.00012	.00000
130	.00943	.01932	.01944	.01143	.00159	.03931	.03505	.00632	.00009	.00000
140	.00825	.01745	.01876	.01271	.00213	.04030	.03479	.00588	.00008	.00000
150	.00712	.01556	.01787	.01392	.00282	.04127	.03451	.00546	.00006	.00000
160	.00605	.01365	.01676	.01503	.00366	.04223	.03419	.00506	.00005	.00000
170	.00506	.01179	.01545	.01595	.00469	.04318	.03386	.00469	.00004	.00000

oxygens. It is not necessary to distinguish between the n and the q terms.

Through the use of exactly this procedure, the data in Table 4 were computed for a number of values both of hydrostatic compression and hydrostatic tension. The numbers given are the number of moles per cubic centimeter of each of the kinds of ions present.

It has been necessary to derive these possible population distributions in the hydrostatic cases before taking up the case of a density gradient such as that which occurs near a discontinuity. It is then assumed that each layer near a discontinuity has one of the population distributions above or an interpolation between two of them. This is discussed in the next section.

III. Conditions Near a Discontinuity

A. Gradient Region

An isotropic liquid does not show viscous flow under the action of a hydrostatic pressure or tension, since such a stress distribution implies no shearing stress across planes of any orientation. In general, one then associates the absence of steady viscous flow in a liquid with the existence of a stress condition that could be described as a hydrostatic compression or tension.

Close to a free surface there is a strong tension in the plane of the surface and zero tension perpendicular to the surface. Such a stress pattern is one that would in general produce viscous flow and yet no flow occurs that would manifest itself by any continuing change in shape. One way out of this difficulty is to say that the liquid is not isotropic (which is perfectly true), but this does not contribute much to describing what is actually going on. It is one of the main purposes of this report to examine, in terms of the postulated model, just how a liquid varies close to a free surface or a liquid–crystal interface and to show that there exist certain ways in which the plane tension (or pressure) can vary with depth so as to produce zero flow. When these variations are then adjusted to satisfy the particular boundary conditions (free surface or liquid–crystal interface), they can then be used to describe the actual structure of the liquid close to the interface and to allow calculation of the surface tension of the liquid or the thickness of the grain boundary in a pure polycrystalline composite.

One way of studying the structure in a varying region is to study the equilibrium conditions between two thin parallel layers less than one bond length apart. The number of bonds of any one kind breaking must be exactly balanced by the number of the same kind reforming.

In the interior of the liquid there are n_6^0 moles per cm^3 of 6-coordinated magnesiums (or oxygens), n_5^0 of 5-coordinated ions, etc. (the superscript refers to the stress-free state), where, according to Table 4,

$$n_6^0 = 0.02535 \text{ moles per cm}^3$$

$$n_5^0 = 0.03425$$

$$n_4^0 = 0.01460$$

$$n_3^0 = 0.00138$$

$$n_2^0 = 0.00002$$

In a layer of thickness dz_1, there are $n_6^0\, dz_1$ 6-coordinated ions per cm^2, $n_5^0 dz_1$ 5-coordinated ions, etc., where dz_1 is considered to be very much smaller than a bond length. Each of the 6-coordinated ions sends out 6 bonds, so that there are $6n_6^0 dz_1$ moles of bonds going out in random directions from this layer and terminating in those layers less than a bond length away on both sides of the dz_1 layer. The number terminating in a neighboring layer of thickness dz_2 will be

$$6n_6^0\, dz_1 \frac{dz_2}{2l}$$

where l is the bond length. This simple result is deduced from the fact that if two parallel planes intersect a sphere, the surface area intercepted between them depends only on their distance apart and not at all on the "latitude" at which the intercept is made. The total number of bonds running from the magnesium ions in the dz_1 layer to the oxygen ions in the dz_2 layer (or vice versa) will be

$$(6n_6^0 + 5n_5^0 + 4n_4^0 + 3n_3^0 + 2n_2^0) \frac{dz_1\, dz_2}{2}$$

or

$$B^0 \frac{dz_1 dz_2}{2}$$

where

$$B^0 = 6n_6^0 + 5n_5^0 + 4n_4^0 + 3n_3^0 + 2n_2^0$$

Using the values from the stress-free data of Table 4, one obtains $B^0 = 0.38593$.

The surface of a liquid is in plane tension and is therefore in a less dense state than the interior. The material in the interior is stress-free. It seems reasonable that there is a region near the surface where the plane tension is decreasing (exponentially or otherwise) with increasing depth. This region will be examined first, and then we will consider how this region finally terminates in the skin at the surface. The region under the surface will be called the gradient region. In it the plane tension varies with depth, while the normal tension is zero.

A layer of thickness dz_1 in the gradient region will have layers of different density on its two sides. The bonds that it sends out will not go out with random orientation as was the case with a deep interior layer. If bond directions are measured from a normal toward the surface, it is reasonable to assume that the number of bonds within solid angle $d\omega$ at direction θ would be of the form $(P + Q\cos\theta)\, d\omega$.

The total number of bonds going out from the ions of one kind in the dz_1 layer will be

$$2\pi \int_0^\pi (P + Q\cos\theta)\sin\theta\, d\theta = 4\pi P$$

where

$$4\pi P = (6n_6 + 5n_5 + 4n_4 + 3n_3 + 2n_2)\, dz_1 = B dz_1$$

if

$$B = 6n_6 + 5n_5 + 4n_4 + 3n_3 + 2n_2$$

If, at a distance $z_2 (z_2 < l)$ toward the surface, there is a layer of thickness dz_2, then the bonds from the dz_1 layer to the dz_2 layer make an angle θ with the outward normal where

$$\cos\theta = \frac{z_2}{l}$$

and the directions of the bonds from the dz_1 layer to the dz_2 layer lie within a solid angle $d\omega$, where

$$d\omega = 4\pi \frac{dz_2}{2l}$$

The number of bonds to a layer of thickness dz_2 lo- Mg—O or O—Mg) will be

$$\left(P + Q\frac{z_2}{l}\right) 4\pi \frac{dz_2}{2l} = \left(4\pi P + 4\pi Q\frac{z_2}{l}\right)\frac{dz_2}{2l} = \left(B + 4\pi Q\frac{z_2}{l}\right)\frac{dz_2}{2l}$$

The number of bonds to a layer of thickness dz_2 located at $-z_2$ will be

$$\left(B - 4\pi Q\frac{z_2}{l}\right)\frac{dz_2}{2l}$$

This means that in the course of the calculations in the gradient region, if we know the value of B to be assigned to a given layer and we know the number of bonds this layer sends to a neighboring layer on one side, we also know the number it sends to a neighboring layer the same distance away on the other side. This, as will be shown, allows the calculation to proceed layer by layer to give the possible density distribution in a gradient region.

A magnesium ion surrounded by six oxygens can make very little adjustment of the angles between bonds, while a magnesium with fewer than six oxygens can have considerably more freedom in the directions of the bonds.

A layer of thickness dz_1 having $n_6\, dz_1$ 6-coordinated ions per unit area will send

$$6n_6\, dz_1 \frac{dz_2}{2l}$$

bonds from its 6-coordinated magnesiums to a neighboring layer of thickness dz_2. However, the number of bonds from its 5-coordinated magnesiums may be greater than or less than

$$5n_5\, dz_1 \frac{dz_2}{2l}$$

and will be denoted by

$$m_5^{1\text{-}2}\, dz_1 \frac{dz_2}{2l}$$

where the superscript to m refers to the layers interconnected in the order noted. In the stress-free interior,

$m_5^{1-2} = 5n_5^0$, but near the surface or any discontinuity this may not be the case.

The probability that a bond will break or reform will depend on the stress along the direction of the bond. It would actually be more correct to talk in terms of the strain rather than the stress, since it is the slight changes in local geometry that alter the probabilities. However, at this stage of the calculations, where orders of magnitude only are being sought, it is a little easier (although somewhat incorrect) to think in terms of the stress rather than the strain.

The normal stress inside a plane boundary is always taken as zero, since, as far as variations in bond length go, atmospheric pressure is effectively zero. The bonds between two layers one bond length apart are then under zero stress. The probability of their breaking is the same as that of an interior bond, and the probability of two ions coming together to form a new bond will be the same as that of two ions in the interior separated by the same amount.

At some reasonable time after a new surface is formed, the layers near the surface reach some state of structural equilibrium, at which time the number of bonds breaking between two layers is the same as the number reforming between the same two layers. For two layers one bond length apart, so that the bonds are not under stress, the ratio of the probability of a bond of any particular character breaking to the probability of its reforming must be the same as the corresponding ratio for two neighboring layers in the stress-free interior. The entire subsequent treatment of the structure of a gradient region is based on this concept.

It is easier to break a bond between two 6-coordinated ions than between two 2-coordinated ions. The different kinds of bonds must be treated differently and some system of nomenclature must be adopted to describe them. A bond from an a-coordinated ion in layer 1 to a b-coordinated ion in layer 2 will be called an (a—b) bond. Within the limitations of the assumptions already made, the probability of breaking of each of the following bond types will have to be considered:

(6—6)	(5—6)	(4—6)	(3—6)
(6—5)	(5—5)	(4—5)	(3—5)
(6—4)	(5—4)	(4—4)	(3—4)
(6—3)	(5—3)	(4—3)	(3—3)

The probability of a (4—5) bond between two layers breaking will depend first of all on the number of (4—5) bonds per unit area. The number of 4-coordinated ions of either kind in layer 1 is $n_4^1\, dz_1$.

According to the previous definition, the number of bonds going out from these 4-coordinated ions in layer 1 to ions of any coordination number in layer 2 is

$$m_4^{1-2}\, dz_1 \frac{dz_2}{2l}$$

Of these, a fraction will terminate on 5-coordinated ions in layer 2, and this fraction will be the ratio of the number of bonds from 5-coordinated ions in layer 2 to the total number of bonds between the layers. The number of bonds from 5-coordinated ions in layer 2 to layer 1 is

$$m_5^{2-1}\, dz_2 \frac{dz_1}{2l}$$

The total number of bonds between the two layers can be written as either

$$(m_6^{1-2} + m_5^{1-2} + m_4^{1-2} + m_3^{1-2} + m_2^{1-2}) \frac{dz_1\, dz_2}{2l}$$

or

$$(m_6^{2-1} + m_5^{2-1} + m_4^{2-1} + m_3^{2-1} + m_2^{2-1}) \frac{dz_1\, dz_2}{2l}$$

and for convenience will be written

$$B^{1-2} \frac{dz_1\, dz_2}{2l}$$

or

$$B^{2-1} \frac{dz_1\, dz_2}{2l}$$

the order of the two superscripts in this case not being of any significance. The number of (4—5) bonds is then

$$\frac{m_4^{1-2}\, m_5^{2-1}}{B^{1-2}} \frac{dz_1\, dz_2}{2l}$$

and similar expressions can be written for each of the other kinds of bonds. In a gradient region,

$$m_6^{1-2} = 6n_6^1$$

but

$$m_5^{1-2} \neq 5n_5^1$$

$$m_4^{1-2} \neq 4n_4^1$$

$$m_3^{1-2} \neq 3n_3^1$$

$$m_2^{1-2} \neq 2n_2^1$$

In the interior, these inequalities all become equalities.

To reform a (4—5) bond between layer 1 and layer 2, a 3-coordinated magnesium ion in or near layer 1 will have to recombine with a 4-coordinated oxygen in or near layer 2. The number of 3-coordinated magnesium (or oxygen) ions in layer 1 is $n_3^1\,dz_1$ and the number of 4-coordinated oxygen (or magnesium) ions in layer 2 is $n_4^2\,dz_2$.

Now if the distribution of bonds from these 4-coordinated ions were so one-sided that the 4-coordinated ions in layer 2 sent as many bonds to layer 1 as the same number of 6-coordinated ions in layer 2 would do, then none of these 4-coordinated ions in layer 2 would be available to join with ions of any kind in layer 1. Therefore, instead of saying that the probability of the 3-coordinated ion and the 4-coordinated ion is proportional to $n_3^1\,n_4^2$, it is taken as being proportional to $(6n_3^1 - m_3^{1-2})\,(6n_4^2 - m_4^{2-1})$. The ratio of the probability of a (4—5) bond breaking to the probability of a (4—5) bond being reformed between layer 1 and layer 2 is proportional to

$$\frac{m_4^{1-2}\,m_5^{1-2}}{B^{1-2}\,(6n_3^1 - m_3^{1-2})\,(6n_4^2 - m_4^{2-1})}$$

There would also be a temperature-dependent term, but since comparisons will be made with two similar operations at the same temperature, it is not necessary to include this. For the two layers to continue in equilibrium one bond length apart, this expression must be equal to the corresponding expression for two neighboring layers in the stress-free interior. In the interior, the following conditions exist:

$$m_4^{1-2} = 4n_4^0$$

$$m_5^{2-1} = 5n_5^0$$

$$B^{1-2} = B^0$$

$$6n_3^1 - m_3^{1-2} = 6n_3^0 - 3n_3^0 = 3n_3^0$$

$$6n_4^2 - m_4^{2-1} = 6n_4^0 - 4n_4^0 = 2n_4^0$$

Hence

$$\frac{m_4^{1-2}\,m_5^{2-1}}{B^{1-2}\,(6n_3^1 - m_3^{1-2})\,(6n_4^2 - m_4^{2-1})} = \frac{4n_4^0 5n_5^0}{B^0\,3n_3^0 2n_4^0} = \frac{10}{3B^0}\,\frac{n_4^0\,n_5^0}{n_3^0\,n_4^0}$$

All the quantities on the right-hand side have already been computed, so that the left-hand side is known. There are 16 such relations, corresponding to the 16 types of bond that may break. These 16 relations are (remembering that $m_6^{1-2} = 6n_6^1$ and $m_6^{2-1} = 6n_6^2$)

$$\frac{36n_6^1 n_6^2}{B^{1-2}(6n_5^1 - m_5^{1-2})(6n_5^2 - m_5^{2-1})} = \frac{36n_6^0 n_6^0}{B^0 n_5^0 n_5^0} \tag{1}$$

$$\frac{6n_6^1 m_5^{2-1}}{B^{1-2}(6n_5^1 - m_5^{1-2})(6n_4^2 - m_4^{2-1})} = \frac{30n_6^0 n_5^0}{B^0 n_5^0 2n_4^0} \tag{2}$$

$$\frac{6n_6^1 m_4^{2-1}}{B^{1-2}(6n_5^1 - m_5^{1-2})(6n_3^2 - m_3^{2-1})} = \frac{24n_6^0 n_4^0}{B^0 n_5^0 3n_3^0} \tag{3}$$

$$\frac{6n_6^1 m_3^{2-1}}{B^{1-2}(6n_5^1 - m_5^{1-2})(6n_2^2 - m_2^{2-1})} = \frac{18n_6^0 n_3^0}{B^0 n_5^0 4n_2^0} \tag{4}$$

$$\frac{6m_5^{1-2} n_6^2}{B^{1-2}(6n_4^1 - m_4^{1-2})(6n_5^2 - m_5^{2-1})} = \frac{30n_5^0 n_6^0}{B^0 2n_4^0 n_5^0} \tag{5}$$

$$\frac{m_5^{1-2} m_5^{2-1}}{B^{1-2}(6n_4^1 - m_4^{1-2})(6n_4^2 - m_4^{2-1})} = \frac{25n_5^0 n_5^0}{B^0 2n_4^0 2n_4^0} \tag{6}$$

$$\frac{m_5^{1-2} m_4^{2-1}}{B^{1-2}(6n_4^1 - m_4^{1-2})(6n_3^2 - m_3^{2-1})} = \frac{20n_5^0 n_4^0}{B^0 2n_4^0 3n_3^0} \tag{7}$$

$$\frac{m_5^{1-2} m_3^{2-1}}{B^{1-2}(6n_4^1 - m_4^{1-2})(6n_2^2 - m_2^{2-1})} = \frac{15n_5^0 n_3^0}{B^0 2n_4^0 4n_2^0} \tag{8}$$

$$\frac{6m_4^{1-2} n_6^2}{B^{1-2}(6n_3^1 - m_3^{1-2})(6n_5^2 - m_5^{2-1})} = \frac{24n_4^0 n_6^0}{B^0 3n_3^0 n_5^0} \tag{9}$$

$$\frac{m_4^{1-2} m_5^{2-1}}{B^{1-2}(6n_3^1 - m_3^{1-2})(6n_4^2 - m_4^{2-1})} = \frac{20n_4^0 n_5^0}{B^0 3n_3^0 2n_4^0} \tag{10}$$

$$\frac{m_4^{1-2} m_4^{2-1}}{B^{1-2}(6n_3^1 - m_3^{1-2})(6n_3^2 - m_3^{2-1})} = \frac{16n_4^0 n_4^0}{B^0 3n_3^0 3n_3^0} \tag{11}$$

$$\frac{m_4^{1-2} m_3^{2-1}}{B^{1-2}(6n_3^1 - m_3^{1-2})(6n_2^2 - m_2^{2-1})} = \frac{12n_4^0 n_3^0}{B^0 3n_3^0 4n_2^0} \tag{12}$$

$$\frac{6m_3^{1-2} n_6^2}{B^{1-2}(6n_2^1 - m_2^{1-2})(6n_5^2 - m_5^{2-1})} = \frac{18n_3^0 n_6^0}{B^0 4n_2^0 n_5^0} \tag{13}$$

$$\frac{m_3^{1-2} m_5^{2-1}}{B^{1-2}(6n_2^1 - m_2^{1-2})(6n_4^2 - m_4^{2-1})} = \frac{15n_3^0 n_5^0}{B^0 4n_2^0 2n_4^0} \tag{14}$$

$$\frac{m_3^{1-2} m_4^{2-1}}{B^{1-2}(6n_2^1 - m_2^{1-2})(6n_3^2 - m_3^{2-1})} = \frac{12n_3^0 n_4^0}{B^0 4n_2^0 3n_3^0} \tag{15}$$

$$\frac{m_3^{1-2} m_3^{2-1}}{B^{1-2}(6n_2^1 - m_2^{1-2})(6n_2^2 - m_2^{2-1})} = \frac{9n_3^0 n_3^0}{B^0 4n_2^0 4n_2^0} \tag{16}$$

These are not 16 independent relations. From the first five, along with Eqs. (9) and (13), all the rest can be derived. Combining the first four, the following relations can be derived:

$$6n_4^2 - m_4^{2-1} = \frac{4}{10}\frac{n_6^0 n_4^0}{n_5^0 n_5^0}\frac{m_5^{2-1}(6n_5^2 - m_5^{2-1})}{n_6^2} \tag{17}$$

$$6n_3^2 - m_3^{2-1} = \frac{15}{8}\frac{n_5^0 n_3^0}{n_4^0 n_4^0}\frac{m_4^{2-1}(6n_4^2 - m_4^{2-1})}{m_5^{2-1}} \tag{18}$$

$$6n_2^2 - m_3^{2-1} = \frac{16}{9}\frac{n_4^0 n_2^0}{n_3^0 n_3^0}\frac{m_3^{2-1}(6n_3^2 - m_3^{2-1})}{m_4^{2-1}} \tag{19}$$

Equation (1) can be rearranged in the form

$$6n_5^1 - m_5^{1-2} = \frac{B^0}{B^{1-2}}\frac{n_5^0 n_5^0}{n_6^0 n_6^0}\frac{n_6^1 n_6^2}{6n_5^2 - m_5^{2-1}} \tag{20}$$

and Eqs. (1), (5), (9), and (13) give

$$6n_4^1 - m_4^{1-2} = \frac{4}{10}\frac{n_6^0 n_4^0}{n_5^0 n_5^0}\frac{m_5^{1-2}(6n_5^1 - m_5^{1-2})}{n_6^1} \tag{21}$$

$$6n_3^1 - m_3^{1-2} = \frac{15}{8}\frac{n_5^0 n_3^0}{n_4^0 n_4^0}\frac{m_4^{1-2}(6n_4^1 - m_4^{1-2})}{m_5^{1-2}} \tag{22}$$

$$6n_2^1 - m_2^{1-2} = \frac{16}{9}\frac{n_4^0 n_2^0}{n_3^0 n_3^0}\frac{m_3^{1-2}(6n_3^1 - m_3^{1-2})}{m_4^{1-2}} \tag{23}$$

Two adjacent layers (one bond length apart) are chosen from any of the layers in Table 4. One is called layer 1 and the other layer 2. A tentative value is taken for m_5^{2-1}, and $(6n_5^2 - m_5^{2-1})$ is computed.

From Eq. (17), $(6n_4^2 - m_4^{2-1})$ is calculated and, hence m_4^{2-1}.

From Eq. (18), $(6n_3^2 - m_3^{2-1})$ is calculated and, hence, m_3^{2-1}.

From Eq. (19), $(6n_2^2 - m_2^{2-1})$ is calculated and, hence, m_2^{2-1}.

Since

$$B^{1-2} = 6n_6^2 + m_5^{2-1} + m_4^{2-1} + m_3^{2-1} + m_2^{2-1}$$

this can now be calculated and, hence, $(6n_5^1 - m_5^{1-2})$ from Eq. (20). The rest of the equations will give, in turn, m_4^{1-2}, m_3^{1-2}, and m_2^{1-2}.

Since

$$B^{1-2} = 6n_6^1 + m_5^{1-2} + m_4^{1-2} + m_3^{1-2} + m_2^{1-2}$$

this can be calculated again. If it does not agree, the original value of m_5^{2-1} was wrong, and another one is chosen.

The use of a little judgment and the development of simple empirical rules usually mean that not more than three tries are necessary for any pair of adjacent layers.

The values for B^{1-2} and B^2 are then known, and B^{2-3} can therefore be derived since

$$B^{1-2} - B^2 = B^2 - B^{2-3}$$

Layer 3 is then sought, so that when it is placed adjacent to layer 2 (one bond length apart), the number of bonds between them is given by B^{2-3}. This usually means a linear interpolation between two of the layers in Table 4.

For clarity, the process just described in detail could be described in general terms as follows: Two layers one bond length apart are chosen, and any state of plane stress from Table 4 is assigned to each of these layers. The layers are chosen one bond length apart so that the bonds are perpendicular to the surface and hence under zero stress. The processes of breaking and reforming each kind of bond can therefore be directly compared with similar processes between two layers in the stress-free interior. There is then only one pattern of bonds between these two layers that satisfies the equilibrium conditions. The pattern of bonds between the layers uniquely determines the pattern that each of these layers sends out to another layer one bond length away in the other side. This, in turn, uniquely determines the composition and stress of these next layers, and the process can be repeated indefinitely.

Depending on the choice of the first two layers, several different patterns are obtained for the average coordination number plotted against the layer number. If the first two layers are the same and correspond to the stress-free layer in Table 4, then all the other layers will be the same, and this simply gives the state of things in the stress-free interior. This is illustrated in Fig. 3a.

If the two initial layers are of lower average coordination numbers than those in the stress-free state, curves of the type of Fig. 3b may be obtained, which might represent conditions in a thin film with two free surfaces.

If the two initial layers have higher average coordination numbers than those in the stress-free state, curves of the type of Fig. 3c may be obtained, which represent possible conditions on a grain boundary between two crystal grains at temperatures below the melting point of the crystal.

If, in either of the two previous cases, too steep a gradient was assumed to start with, then curves of the type of Fig. 3d may be obtained, which "cross the line." These might represent a random layer in the surface of a crystal grain at a temperature near the melting point.

If the first two layers are very carefully chosen, then a distribution like that of Fig. 3e or 3f may be obtained. Figure 3e represents conditions as the free liquid surface is approached from the stress-free interior, and Fig. 3f represents conditions in which a liquid–crystal interface is approached from the interior of the liquid at a temperature at which the crystal is at equilibrium with the liquid. All these are possible, depending on the exact boundary conditions imposed in any particular case.

B. Free Surface

One way of describing a free surface is as follows: The ions in and close to the surface send bonds only in the inward direction so that a 6-coordinated ion on the surface is a complete impossibility and even a 5- or 4-coordinated ion is unlikely. The assumption is then made that the skin layer is populated by 2- and 3-coordinated ions. The number of bonds they send to a layer one bond length below the surface is as if the surface layer had 4- and 6-coordinated ions, but their affinity for other ions is more like the affinity of 2- and 3-coordinated ions. The skin layer should really be thought of as having a finite thickness of some small fraction (say 10% or less) of a bond length. The exact thickness of this layer is not actually important in the free surface, but it is important at a liquid–crystal interface.

It should be pointed out, if it is not immediately obvious, that this method of describing the surface is not a rigorously complete description of what is happening

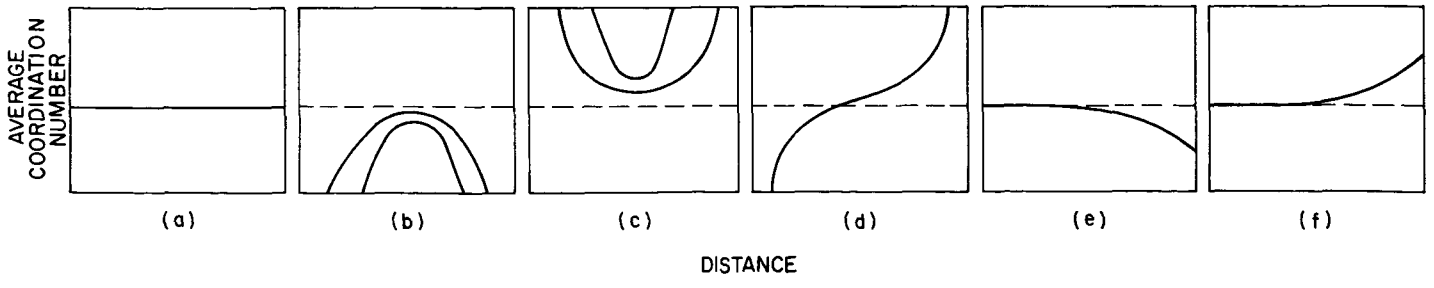

Fig. 3. Possible types of density gradient as a function of selection of ratio of average coordination in first two layers: (a) ratio equal to stress-free state (stress-free layer), (b) ratio less than stress-free state, (c) ratio greater than stress-free state, (d) ratio much less or much greater than stress-free state, (e), (f), ratio selected for distributions shown.

close to the surface of a liquid. It fails to account completely for the behavior of the layers less than one bond length from the surface. In this region the number of 6-, 5-, and 4-coordinated ions is gradually increasing, going in from the surface. This certainly can be treated with much greater sophistication. The present approach is designed to give a preliminary feeling for some of the orders of magnitude involved and seems to be capable of doing this.

Within the limits of the assumptions made, the problem is then to express as precisely as possible the conditions for equilibrium between the surface layer and a layer one bond length below the surface. Each 2-coordinated ion in the surface can combine with any available ion in the interior layers to become a 3-coordinated ion. The bonds to each 3-coordinated ion in the surface may, on occasion, break. For equilibrium, the two processes of breaking and reforming must balance.

The surface layer is called layer 1 and is of thickness dz_1. It contains $n_3^1\,dz_1$ 3-coordinated ions and $n_2^1\,dz_1$ 2-coordinated ions of either charge per unit area. The $(3n_3^1 + 2n_2^1)\,dz_1$ bonds emanating from these ions all go inward but are assumed to have perfectly random orientations within the solid angle of 2π covering all the inward directions; this means that the number of bonds going to a layer of thickness dz_2 within one bond length l is

$$(3n_3^1 + 2n_2^1)\,dz_1\,\frac{dz_2}{l}$$

or

$$(6n_3^1 + 4n_2^1)\,dz_1\,\frac{dz_2}{2l}$$

or

$$B^{1\text{-}2}\,\frac{dz_1\,dz_2}{2l}$$

where

$$B^{1\text{-}2} = 6n_3^1 + 4n_2^1 = B^{2\text{-}1}$$

and in the notation used before

$$m_3^{1\text{-}2} = 6n_3^1$$

$$m_2^{1\text{-}2} = 4n_2^1$$

The assumption of what is meant by the random orientation of bonds from the surface layer is discussed in greater detail in Appendix C.

The bonds from the 3-coordinated ions in the surface will divide themselves among the 6-, 5-, 4-, 3-, and 2-fold ions in layer 2, one bond length below the surface, in a manner depending on the number of bonds each of these ions in layer 2 sends to layer 1. The number of (3—6) bonds is then

$$6n_3^1\,\frac{dz_1\,dz_2}{2l}\,\frac{m_6^{2\text{-}1}}{B^{1\text{-}2}} = 6n_3^1\,\frac{dz_1\,dz_2}{2l}\,\frac{6n_6^2}{B^{1\text{-}2}}$$

The number of (3—5) bonds is

$$6n_3^1\,\frac{dz_1\,dz_2}{2l}\,\frac{m_5^{2\text{-}1}}{B^{1\text{-}2}}$$

The number of (3—4) bonds is

$$6n_3^1\,\frac{dz_1\,dz_2}{2l}\,\frac{m_4^{2\text{-}1}}{B^{1\text{-}2}}$$

The number of (3—3) bonds is

$$6n_3^1\,\frac{dz_1\,dz_2}{2l}\,\frac{m_3^{2\text{-}1}}{B^{1\text{-}2}}$$

These are the bonds whose possible breaking enters into the balance of breaking and reforming.

The probability of a 2-coordinated ion in layer 1 combining with a 5-coordinated ion in layer 2 will be taken, as in the earlier case, to be proportional to

$$(6n_2^1 - m_2^{1\text{-}2})\,(6n_5^2 - m_5^{2\text{-}1})$$

and the ratios of this probability to the probability of breaking of a (3—6) bond must, at the same temperature, be the same as the corresponding ratio for two adjacent layers (less than one bond length apart) within the interior of the stress-free liquid:

$$\frac{6n^1_3 6n^2_6}{B^{1-2}(6n^1_2 - m^{1-2}_2)(6n^2_5 - m^{2-1}_5)} = \frac{3n^0_3 6n^0_6}{B^0 4n^0_2 n^0_5}$$

The corresponding relations for each of the other kinds of bonds are, using the same principles,

$$\frac{6n^1_3 m^{2-1}_5}{B^{1-2}(6n^1_2 - m^{1-2}_2)(6n^2_4 - m^{2-1}_4)} = \frac{3n^0_3 5n^0_5}{B^0 4n^0_2 2n^0_4}$$

$$\frac{6n^1_3 m^{2-1}_4}{B^{1-2}(6n^1_2 - m^{1-2}_2)(6n^2_3 - m^{2-1}_3)} = \frac{3n^0_3 4n^0_4}{B^0 4n^0_2 3n^0_3}$$

$$\frac{6n^1_3 m^{2-1}_3}{B^{1-2}(6n^1_2 - m^{1-2}_2)(6n^2_2 - m^{2-1}_2)} = \frac{3n^0_3 3n^0_3}{B^0 4n^0_2 4n^0_2}$$

These relations may be written as follows:

$$6n^2_5 - m^{2-1}_5 = n^2_6\left[\frac{n^1_3}{B^{1-2}(6n^1_2 - m^{1-2}_2)}\frac{2n^0_2 n^0_5}{n^0_3 n^0_6}\right]$$

$$6n^2_4 - m^{2-1}_4 = m^{2-1}_5\left[\frac{n^1_3}{B^{1-2}(6n^1_2 - m^{1-2}_2)}\frac{4B^0}{5}\frac{n^0_2 n^0_4}{n^0_3 n^0_5}\right]$$

$$6n^2_3 - m^{2-1}_3 = m^{2-1}_4\left[\frac{n^1_3}{B^{1-2}(6n^1_2 - m^{1-2}_2)}\frac{3B^0}{2}\frac{n^0_2 n^0_3}{n^0_3 n^0_4}\right]$$

$$6n^2_2 - m^{2-1}_2 = m^{2-1}_3\left[\frac{n^1_3}{B^{1-2}(6n^1_2 - m^{1-2}_2)}\frac{8B^0}{3}\frac{n^0_2 n^0_2}{n^0_3 n^0_3}\right]$$

The first step is to assume some arbitrary ratio of $n^1_3 : n^1_2$ in the surface layer. It is then assumed that the surface layer behaves as if it were a slice of thickness dz_1 out of a large homogeneous volume containing 3- and 2-coordinated ions in the assumed ratio and that a 3-coordinated ion occupies a volume of 11.907 cm^3 per mole and a 2-coordinated ion occupies 16.796 cm^3 per mole as in the interior calculations. This means that once the ratio is chosen, the absolute values of n^1_3 and n^1_2 are known and hence everything within the square brackets in the four equations is known. If n^2_6, n^2_5, n^2_4, n^2_3, and n^2_2 are assumed to have one of the sets of values previously calculated or some interpolated set, then each of the quantities m^{2-1}_5, m^{2-1}_4, m^{2-1}_3, and m^{2-1}_2 can be calculated, and hence B^{1-2} can also, since

$$B^{1-2} = 6n^2_6 + m^{2-1}_5 + m^{2-1}_4 + m^{2-1}_3 + m^{2-1}_2$$

and this value must be the same as the value given by the relation

$$B^{1-2} = 6n^1_3 + 4n^1_2$$

The single assumption of the ratio of $n^1_3 : n^1_2$ in the surface layer uniquely determines the layer one bond length below. If we know the nature of this layer and the number of bonds it sends to the surface layer, we also know the number of bonds it sends to the layer one bond length further in. This next layer is thus uniquely determined, and so on. This succession of layers must asymptotically approach the stress-free interior condition, and there is only one choice of surface layer that allows this to happen.

With the assumptions that have been made, the one and only surface layer that corresponds to the asymptotic

distribution consists of 98.17% 3-fold ions and 1.83% 2-fold ions. These values were found by trial and error. Values on one side of this give rise to a curve of the type of Fig. 3b and, on the other side, to a curve of the type of Fig. 3d.

The layer one bond length below the surface has an average coordination number of 4.609. The next layer below has 4.999. The succeeding layers are all very close to the value of 5.105 existing in the stress-free interior of the liquid. A rough numerical integration shows that this corresponds to a surface tension of about 2700 dynes per centimeter, which is probably too large by about a factor of 2. Considering the nature of the assumptions made along the way, this is not considered a discouraging result.

C. Liquid–Crystal Interface

The study of the free surface is not a prime objective of this investigation but is a useful starting point for the study of the interface between a crystal and a liquid. At the melting point of the crystal, the crystal surface can exist in equilibrium with an infinite thickness of liquid. Probably if the theory were sufficiently well developed, different melting points might even be assigned to different faces, but none of the parameters are as yet sufficiently well known to allow such distinctions to be made. In order to get some numbers to use in the calculations, a crystal face will be taken as meaning a (100) face.

If liquid MgO is brought into contact with a (100) face of a crystal of MgO, a certain number of the ions in the liquid will bond themselves to the surface ions of the crystal with the same kind of ionic forces as hold either the crystal or the liquid together. The interface will then be described as follows: It will be essentially the same as the free surface except that to a number of the ions in the surface there will be bonds, essentially perpendicular to the surface, which will bond the ions of the liquid surface layer to the ions of the crystal surface. If more of these bonds are forming than are breaking, the crystal will be growing, and if more are breaking than forming, the crystal will be dissolving. At equilibrium there will be a balance, and the conditions for balance help to determine the nature of the surface layer.

The free surface of the liquid was considered to consist of ions that are bonded to two or to three ions of the opposite charge in the liquid. If these ions may now be given an extra bond, joining them to the crystal, there will be essentially four kinds of ions to be considered, since each of the two previous species may or may not be bonded to the crystal. This really implies a finite thickness for the surface layer since an ion not bonded to the crystal will, of necessity, be further from the crystal face than one that is so bonded. This layer of finite thickness is also forced on us for other reasons, as will appear shortly.

The four types of ions, (a), (b), (c), and (d), are illustrated in Fig. 4 and listed below.

(1) Type (a) is joined to three ions in the liquid and to one in the crystal surface.

(2) Type (b) is joined to three ions in the liquid but not bonded to the crystal.

(3) Type (c) is joined to two ions in the liquid and to one in the crystal surface.

(4) Type (d) is joined to two ions in the liquid but not bonded to the crystal.

The number of moles per unit volume of each of these is denoted by n_a, n_b, n_c, and n_d respectively.

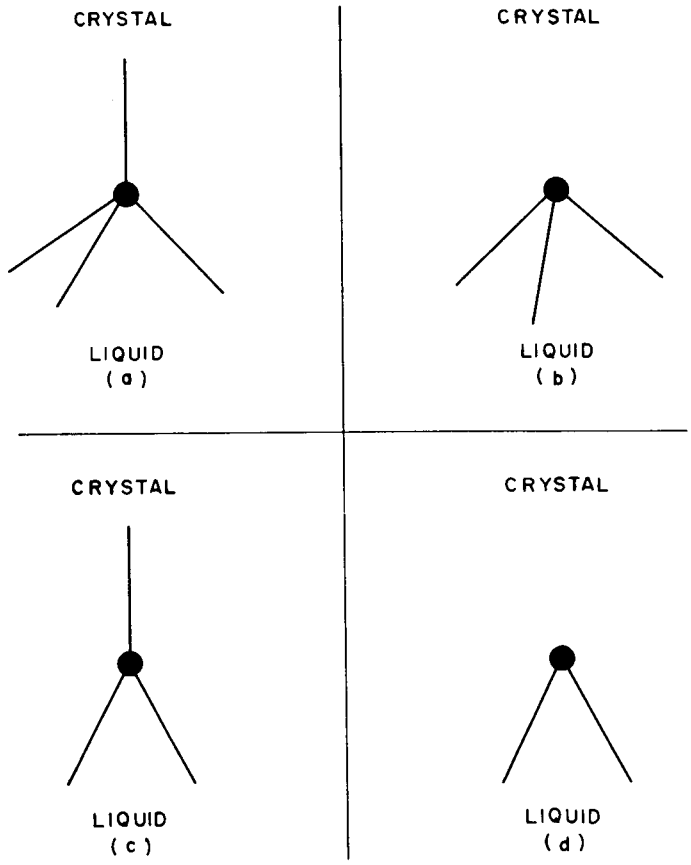

Fig. 4. Different bonding types of ions in surface layer

The surface layer must be in equilibrium with the crystal surface and with each liquid layer lying within one bond length, or in these calculations the surface layer must be in equilibrium with the particular layer lying one bond length below the surface. Two layers are in equilibrium if the number of bonds of any one species joining them remains constant because of equal rates of breaking and reforming. Since the normal stress is zero, the bonds between layers one bond length apart are in zero stress, and the rates of breaking and reforming can be directly compared with the corresponding rates between any two layers in the interior of the stress-free liquid.

The number of either cations or anions per unit area of the crystal surface is denoted by n_s, which is easily computed for any particular face. In most of the calculations, the crystal face was assumed to be a (100) face. This face is easier to handle than most of the other possible faces, but any orientation could be handled with a little more effort. The condition for equilibrium is that the number of bonds of any one kind between the layers divided by the product of the concentration in each of the layers of those kinds of ions whose coming together would reform the bond in question must be the same as the same ratio for two adjacent layers in the stress-free interior.

If the surface layer is assumed to have thickness Δl, then in this layer there are $n_a \Delta l$ ions of type (a) per unit area and $n_c \Delta l$ ions of type (c) per unit area; therefore, between the liquid and the crystal there are $(n_a + n_c)\Delta l$ bonds per unit area. There are, therefore, in the crystal surface, $n_s - (n_a + n_c)\Delta l$ cations (or anions) not connected to the liquid, and any one of these is available to join with a (b) or a (d) ion in the liquid surface and form a new bond.

The number of ions of type (b) in the liquid surface is $n_b \Delta l$ and, of type (d), is $n_d \Delta l$.

There are two kinds of bonds between the liquid and the crystal, and these could be designated as (a—6) bonds and (c—6) bonds, meaning that they connect an (a) type or a (c) type ion in the liquid surface to a 6-coordinated ion in the crystal surface. The ratio of the concentration of (a—6) bonds to the product of the concentration in the layers of ions capable of joining together to form (a—6) bonds is

$$\frac{n_a \Delta l}{n_b \Delta l\,[n_s - (n_a + n_c)\Delta l]}$$

or

$$\frac{n_a}{n_b\,[n_s - (n_a + n_c)\Delta l]}$$

The corresponding ratio for (c—6) bonds is

$$\frac{n_c}{n_d\,[n_s - (n_a + n_c)\Delta l]}$$

To compare these quantities with similar quantities for two adjacent interior layers, a (b) type ion is taken to have the same tendency to recombine with other ions as a 3-coordinated ion, a (d) type ion is taken to behave like a 2-coordinated ion, and an (a—6) bond is taken to have the same tendency to break as a (4—6) bond, while a (c—6) bond behaves like a (3—6) bond.

The number of (4—6) bonds between a layer of thickness dz_1 and an adjacent layer of thickness dz_2 in the interior is

$$\frac{4n_4^0 6n_6^0}{B^0}\frac{dz_1\,dz_2}{2l}$$

where

$$B^0 = 6n_6^0 + 5n_5^0 + 4n_4^0 + 3n_3^0 + 2n_2^0$$

as was shown earlier. The number of available 3-coordinated ions in layer 1 was taken to be proportional to $(6n_3^1 - m_3^{1\text{-}2})\,dz_1$, but for comparison with the case in question, this should be written

$$\left(n_3^1 - \frac{m_3^{1\text{-}2}}{6}\right)dz_1$$

Similarly, the available 5-coordinated ions in layer 2 should be written

$$\left(n_5^2 - \frac{m_5^{2\text{-}1}}{6}\right)dz_2$$

In the interior, n_3^1 can be written as n_3^0; n_5^2 as n_5^0; $m_3^{1\text{-}2}$ as $3n_3^0$; and $m_5^{2\text{-}1}$ as $5n_5^0$. Hence,

$$\frac{n_a}{n_b\,[n_3 - (n_a + n_c)\Delta l]} = \frac{\dfrac{4n_4^0 6n_6^0}{B^0}\dfrac{dz_1\,dz_2}{2l}}{\dfrac{1}{36}3n_3^0 n_5^0\,dz_1\,dz_2} = \frac{288}{2l}\frac{n_4^0}{n_3^0}\frac{n_6^0}{n_5^0}\frac{1}{B^0}$$

and

$$\frac{n_c}{n_a\,[n_s - (n_a + n_c)\,\Delta l]} = \frac{\dfrac{3n_3^0\,6n_6^0}{B^0}\,\dfrac{dz_1\,dz_2}{2l}}{\dfrac{1}{36}\,4n_2^0\,n_5^0\,dz_1\,dz_2} = \frac{162}{2l}\,\frac{n_3^0}{n_2^0}\,\frac{n_6^0}{n_5^0}\,\frac{1}{B^0}$$

These two equations and the relation

$$2\,(n_a\,v_a + n_b\,v_b + n_c\,v_c + n_d\,v_d) = 1$$

(where v is the volume in cubic centimeters per mole to be assigned to these ions) give three equations to determine the four quantities n_a, n_b, n_c, and n_d. If one of them is chosen arbitrarily, all of the rest are determined. If, for instance, n_a is taken as 0.04000, $n_b = -0.00017$, $n_c = 0.04226$, and $n_d = -0.00004$. Other choices of n_a give similar patterns, in that n_b is always very much smaller than n_a, and n_d is very much smaller than n_c. This means that almost all the ions in the surface layer are bonded to the crystal surface. As a first approach it was assumed, then, that the surface layer consisted entirely of (a) and (c) type ions. The relative amount of each of these is determined at the melting point by the condition that the gradient within the liquid is of the asymptotic type, so that the density blends into that of the stress-free condition as the distance from the crystal increases.

There is only one ratio of n_a to n_c that gives this condition, and for the particular numerical values of the various parameters that have been used here, this ratio is about 60.75% of (a) type to 39.25% (c) type. At this value, the density comes very close to the interior density about three or four bond lengths from the interface.

The same assumed energy relations were assumed to hold at lower temperatures and it was calculated that at 100°C below the melting point the asymptotic distribution did not exist any longer, but rather that the density decreased to a minimum and then increased again, so that at this temperature the liquid could exist in a thickness of about two bond lengths between two crystal grains. While this is a somewhat tentative result, considering many of the gross oversimplifications, it does seem to indicate that the grain boundary thickness in pure MgO must be quite small in terms of bond lengths.

IV. Discussion of Method and Results

More rigorous development of this theory is possible with the aid of electronic computing facilities. Any of the few numerical computations that were attempted assumed an almost perfect interchangeability of anions and cations, although this was not a limitation on the basic theory, which treated the two ions and the energies involved quite distinctly. It is difficult to put more than six oxygens around a magnesium, but geometrically there is no difficulty in putting six magnesiums around an oxygen. If only for this reason, it will be desirable to attempt to evaluate those parameters that will accurately describe the differences between the ions. This will be particularly important at the surface, where it is very often assumed that the more polarizable anions protrude beyond the cations.

One or two actual contradictions are introduced for the sake of simplicity. It was considered meaningful to talk about two layers one bond length apart but, in the calculation of the volume occupied by ions of different coordination numbers, to make use of the well recognized fact that the bond distance is a function of coordination number. In other words, it will be necessary to learn how to handle bonds of different lengths. This will be particularly true when dealing with mixed oxides and will probably be handled by paying much more attention to the details of the elasticity problems involved. Between two adjacent layers there will be bonds of different lengths and, therefore, different orientations and different states of stress and strain. When the theory is better able to specify how the state of stress and strain of the bonds of all kinds that have their midpoints in a given plane varies with orientation, then it should be possible to handle mixed oxides as well as the obvious variations in bond length present in a single oxide.

With the ability to handle several different cations, the problem of the effect of hydroxyl ions as an impurity could be treated. Since any additives will lower the liquidus and since the grain boundary thickness decreases from infinity at the temperature where the pure MgO crystals are in equilibrium with the liquid, it is reasonable to guess that the presence of impurities will increase the equilibrium thickness of the grain boundaries. It is impossible to put orders of magnitude in the variation at this time but the theory might be able to treat this.

Since the theory has developed methods to describe the probability of the breaking and reforming of bonds under different temperatures and stress conditions and also the volume changes to be associated with such processes, it should be possible to calculate viscosities of simple oxide melts and mixtures of melts. The same ideas are currently being applied only to silicate melts but might also give valuable information on melts currently of importance in the fused–cast refractory industry.

Appendix A

Validity of Network Energy Calculations

The assumption is made that in a network it is valid to calculate molar energies by taking the numbers in Table 1 as representing, when multiplied by e^2/r, the potentials existing at the locations of ions of the different coordination numbers, multiplying these by the charge on the ions of such surroundings, adding over the whole structure, and dividing by 2. As a check on the validity of such a calculation for a network, it is interesting to apply the same concept to the calculation of energies of crystal structures other than those from which Table 1 was derived.

Rutile (TiO_2), for example, has, per molecule, one titanium ion of charge 4 and two oxygen ions of charge -2. Each titanium ion is surrounded by six oxygen ions and each oxygen ion is surrounded by three titanium ions.

Since each oxygen has a charge of -2, the potential at the location of a titanium ion ϕ_{Ti} may be written

$$\phi_{Ti} = -2 \times 1.748 \frac{e^2}{r}$$

Since the charge in the titanium has the value $+4$,

$$e_{Ti}\,\phi_{Ti} = -4 \times 2 \times 1.748 \frac{e^2}{r}$$

or $-13.984\,e^2/r$. In the same way, ϕ_O may be written

$$\phi_O = 4 \times 1.538 \frac{e^2}{r}$$

The value of 1.538 is read from the curve of values for the Madelung constant as a function of coordination numbers:

$$e_O\,\phi_O = -2 \times 4 \times 1.538 \frac{e^2}{r}$$

or $-12.304\,e^2/r$. The energy per molecule is then

$$-\frac{1}{2}\frac{e^2}{r}[13.984 + (2 \times 12.304)] = 19.296 \frac{e^2}{r}$$

The directly calculated Madelung constant for rutile is 4.816, which, according to the conventions usually used, means that a crystal of the rutile structure made up of cations with charge $+2$ and anions of charge -1 would have an energy of $4.816\,e^2/r$ ergs per molecule.

Since the charges are twice these standard values, the charge per molecule is four times this or $19.264\,e^2/r$, in very good agreement with the less rigorous method used above.

For corundum (Al_2O_3), the method used above gives $24.330\,e^2/r$, compared with $25.031\,e^2/r$ by direct Madelung constant determination.

The same method applied to the fluorite (CaF_2) structure gives $5.048\,e^2/r$, compared with $5.0388\,e^2/r$ by direct Madelung constant calculation.

Such reasonably good agreement on these crystals of mixed valence lends considerable plausibility to the calculation of energies of a random network using the same principles.

Appendix B

Effect of Randomness

One way of attempting to describe some of the difference between a regular crystal lattice and a random network is to say that in the crystals all of the various interionic distances are rigorously fixed by the geometry, while in a network the near neighbors are fairly well fixed as far as distance from any arbitrarily chosen central ion are concerned but that more and more latitude is allowed in distances from the central ion as these distances increase. Instead of saying that there is a certain number of ions at some definite distance, one would say rather that there is a certain probability of finding ions at or near this distance, normalizing this probability to correspond to the actual number of ions involved. The function describing this probability would be one that goes to zero at $r = 0$ and also at $r = \infty$ but has a peak at the value of r corresponding to a regular crystal structure.

Instead of saying that there was a charge q (the sum of the charges of all ions at one specific distance r) at some distance r, the idea would be expressed by saying that the probability of finding charge between r and $r + dr$ would be expressed by

$$\frac{q}{\sigma r_0 e^{(\sigma^2)/4} \pi^{1/2}} \exp\left[- \frac{\left(\ln \frac{r}{r_0}\right)^2}{\sigma^2} \right] dr$$

where the particular form has been chosen to have a maximum at $r = r_0$, to go to zero at $r = 0$ and $r = \infty$, and to satisfy the relation

$$\int_0^\infty \frac{q}{\sigma r_0 e^{(\sigma^2)/4} \pi^{1/2}} \exp\left[- \frac{\left(\ln \frac{r}{r_0}\right)^2}{\sigma^2} \right] dr = q$$

The quantity σ expresses the lack of sharpness of the distribution $\sigma = 0$ corresponding to a crystalline distribution.

The potential ϕ at the central ion from such a distribution would be given by

$$\phi = \frac{q}{\sigma r_0 e^{(\sigma^2)/4} \pi^{1/2}} \int_0^\infty \exp\left[- \frac{\left(\ln \frac{r}{r_0}\right)^2}{\sigma^2} \right] \frac{1}{r} dr$$

which becomes

$$\frac{q}{r_0} \exp\left(- \frac{\sigma^2}{4} \right)$$

and has the effect of reducing ϕ in a manner dependent on σ. This not very surprising result really arises from the particular form of the distribution selected. Because the distribution must go to zero at $r = 0$, it is not quite symmetrical about $r = r_0$ and, in fact, pushes the charge a little away from the value r_0; in this way it reduces the contribution.

Since it seems to be the case in random networks that have been extensively studied that the interionic distances for near neighbors are essentially the same for glasses as for crystals, the value of σ is considered to be small enough so that the randomness will not seriously affect the calculations.

Appendix C

Orientation of Bonds From Surface Layers

In the preceding calculation, the assumption was very explicitly made that the bonds emanating from the surface layer went out with a random orientation and that this implied that the number within any inward-directed solid angle $d\omega$ was simply proportional to $d\omega$ and independent of its orientation. If it is postulated that no two bonds going out from the same ion can make an angle of less than 90 deg with each other and that all combinations of directions not violating this restriction are equally probable, then it is possible, as will be shown below, to calculate what the distribution with angle will be. This distribution turns out to be very different from the so-called random distribution used in the calculations. In fact, as the angle that the bond makes with the surface plane approaches 90 deg, the probability of finding a bond in that direction approaches zero. This is shown below, first for the case of a surface ion with two bonds, and then for one with three.

I. Surface Ion With Two Bonds

It is assumed that there are, in the surface, N ions per unit area, each connected to two ions of the opposite charge. The two bonds have been labeled, purely at random regardless of orientation, number 1 and number 2. The distribution with angle of the number 1 bonds will therefore be exactly the same as the distribution of number 2 bonds. Every pair of directions lying within the inward hemisphere but not closer to each other than 90 deg is equally probable according to the assumption.

If the number 1 bond makes an angle of θ with the surface inward normal, then the number 2 bond has its direction restricted to a lune on the sphere surrounding the ion concerned. This lune is bounded by two great circles intersecting each other at an angle θ and subtends a solid angle of 2θ at the central ion. Since all directions within this lune are equally probable, this means that the probability of finding a number 1 ion at angle θ is proportional to 2θ or simply to θ. This means that the number of number 1 bonds within solid angle $d\omega$ at angle θ to the inward normal is $A\theta\, d\omega$, where A is an undetermined constant that must satisfy the condition that the integral of this expression over the whole inward hemisphere must be equal to N or

$$2\pi A \int_0^{\pi/2} \theta \sin\theta\, d\theta = N$$

or

$$A = \frac{N}{2\pi}$$

The number of number 1 bonds in solid angle $d\omega$ at angle θ with the inward normal is

$$\frac{N}{2\pi}\theta d\omega$$

which implies that the concentration at $\theta = 0$ is zero. One way of handling this difficulty is to assign to the surface layer a finite thickness Δl (much less than the bond length l) and to assume that each ion within this layer sends out bonds with the same distribution as that just calculated.

A layer of thickness dz_2 collects from a neighboring layer, less than one bond length away, all bonds lying within a solid angle:

$$4\pi \frac{dz_2}{2l}$$

or

$$\frac{2\pi\, dz_2}{l}$$

and these bonds make with the inward normal an angle whose cosine is

$$\frac{z_2 - z_1}{l}$$

The bonds from a layer z_1 inside the surface going to a layer one bond length from the surface make with the inward normal an angle whose cosine is

$$\frac{l - z_1}{l}$$

The number of bonds from a layer of thickness dz_1, distance z_1 in from the surface, and terminating in a

layer of thickness dz_2 one bond length in from the surface, is then

$$\frac{n_2\,dz_1}{2\pi}\cos^{-1}\frac{l-z_1}{l}\frac{2\pi\,dz_2}{l}$$

or

$$n_2\,dz_1\cos^{-1}\frac{l-z_1}{l}\frac{dz_2}{l}$$

where n_2 is the number of ions per unit volume on the surface layer, and the total number terminating in this same layer from all of the layers within Δl of the surface is

$$n_2\,dz_2\int_0^{\Delta l}\cos^{-1}\frac{l-z_1}{l}\frac{dz_1}{l}$$

By writing

$$\theta=\cos^{-1}\frac{l-z_1}{l}$$

this becomes

$$n_2\,dz_2\int_0^{\cos^{-1}(l-\Delta l)/l}\theta\sin\theta\,d\theta$$

If $\Delta l/l$ is taken as 0.1, this becomes $0.03\,n_2\,dz_2$. Since there are two bonds from each of these surface ions, the total number of bonds from this surface layer to a layer of thickness dz_2, one bond length from the surface, is $0.06\,n_2\,dz_2$.

II. Surface Ion With Three Bonds

The problem is a little more involved when there are three bonds instead of two. Again, these are taken to have been labeled number 1, number 2, and number 3 for each ion in a perfectly random manner. If the number 1 bond makes angle θ_1 with the inward normal, then both the number 2 and number 3 bonds are located within a lune formed by two great circles intersecting at angle θ_1. If the position of the number 2 bond is now selected within this lune, then the position of the number 3 bond is further limited to a spherical triangle, two of whose sides are the great circles bounding the lune, while the other is a great circle whose pole is the location of the number 2 bond. The probability of finding a number 1 bond in a given position will be obtained by evaluating an integral in which the location of the number 2 bond is allowed to traverse appropriate orientations. These orientations are defined by the position of the number 1 and number 2 bond locations and are associated with a factor equal to the area of the spherical triangle available to the number 3 bond.

To evaluate this integral, consider a lune bounded by $\phi=0$ and $\phi=\theta_1$. If bond number 2 is located at a direction $\theta\phi$ within this lune ($0\leq\phi\leq\theta_1$), then the spherical triangle available to bond 3 may be computed, remembering that the area of a spherical triangle is equal to the sum of the three interior angles minus π and that the angle of intersection of two great circles is the same thing as the angular distance between their poles. The area is then

$$\cos^{-1}(\sin\theta\sin\phi)+\cos^{-1}[\sin\theta\sin(\theta_1-\phi)]+\theta_1-\pi$$

The integral to be evaluated is

$$\int_0^{\theta_1}\int_0^{\pi}\{\cos^{-1}(\sin\theta\sin\phi)+\cos^{-1}[\sin\theta\sin(\theta_1-\phi)]+\theta_1-\pi\}\sin\theta\,d\theta\,d\phi$$

and the probability of finding a number 1 bond lying within a solid angle $d\omega$ located at direction θ_1 is proportional to this times $d\omega$.

This expression was integrated numerically and the results are shown in Table C-1, expressed as the percentage of the bonds that lie at an angle of less than those values listed. For comparison, the same percentages are also shown for ions with two bonds and ions with one bond (perfectly random).

Table C-1. Possible angular distribution of bonds to a surface ion

Angular limits, from 0 to angle listed, deg	Percentage of bonds within listed limits		
	3 bonds	2 bonds	1 bond
9	.02	.13	1.23
18	.26	1.03	4.89
27	1.15	3.42	10.90
36	3.35	7.95	19.10
45	7.67	15.17	29.29
54	15.09	25.50	41.22
63	26.87	39.18	54.60
72	43.98	56.27	69.09
81	67.90	76.65	84.35
90	100.00	100.00	100.00

The restrictions on the smallest angle between bonds (90 deg) have the effect of greatly changing the distribution. Again it is necessary to postulate a certain thickness of surface layer, and if this is taken again as 0.1 l, then the number of number 1 bonds from the surface layer to a layer of thickness dz_2 one bond length from the surface is $0.01\, n_3\, dz_2$, and the total number of bonds will be $0.03\, n_3\, dz_2$.

III. Bonds at Right Angles

If it is specified that the two bonds to a surface ion are perpendicular to each other, then for each choice of the orientation of bond number 1 the second bond may be located anywhere on a semicircle that is half of the great circle of which bond number 1 is the pole. Regardless of the orientation of bond number 1, the semicircle is the same size; hence, all orientations of bond number 1 are equally probable and all orientations of bond number 2 are also equally probable.

The same argument holds equally well for three bonds instead of two. This means that there is quite a range of distribution possible, from the distribution in which the bonds are always mutually perpendicular to the one in which they are random. Specification of the relative amounts of 2- and 3-coordinated ions in a free surface is not enough to describe the surface completely, and some other condition must be developed to specify the orientational distribution of the bonds. The most likely will be the condition that the surface layer has to be in equilibrium with itself, which means that the number of bonds breaking entirely within the layer is equal to the number reforming under whatever state of plane tension or compression the layer adjusts itself to. This still remains to be investigated in much more detail.